Bimetallic Oxidation Catalysts. Synthesis, X-ray Analysis, and Reactivity of a Binuclear p-Hydroquinone-Containing Copper(II) Complex

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possible electronic states in these groups. Subsequent terms represent analogous ET percolation routes through all combinations of bridge groups and their different electronic states.

If only nearest-neighbor interactions are important, eq A.17 is drastically simplified. Only a single group of terms remains, namely the Nth order term

$$T_{DA} = \sum_{\alpha}\sum_{\beta}\cdots\sum_{\xi} \frac{V_{D,(B1)}^{(1)} V_{(B1)\beta,(B2)\gamma}^{(1)} \cdots V_{(BN)\xi,A}^{(1)}}{(E_D - E_{(B1)\beta})(E_D - E_{(B2)\gamma})\cdots(E_D - E_{(BN)\xi})} \quad (A.18)$$

where $V_{D(B1)\beta}^{(1)} \equiv \langle \Phi_D | V | \Phi_{(B1)\beta} \rangle$, etc. In principle eq A.18 incorporates all conceivable combinations of superexchange and hole transfer mechanisms. If furthermore only a single electronic state on each bridge group contributes, then T_{DA} is further reduced, giving

$$T_{DA} = V_{DA}^{(N)} = \frac{V_{D(B1)}^{(1)} V_{(B1)(B2)}^{(1)} \cdots V_{(BN)A}^{(1)}}{(E_D - E_{B1})(E_D - E_{B2})\cdots(E_D - E_{BN})} \quad (A.19)$$

which is the form used in eq 8 and in the extended Hückel calculations.

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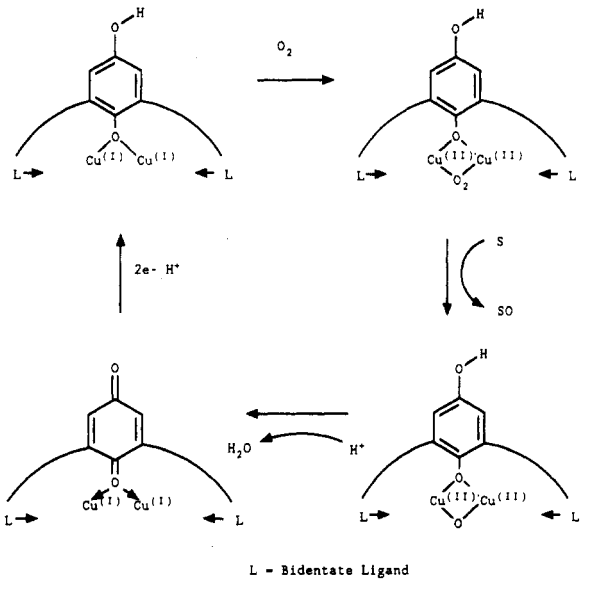
The new pentadentate ligand 1,3-bis[*N*-2-(2'-pyridylethyl)formimidoyl]-2,5-dihydroxybenzene (**1**) was prepared in five steps from 2,6-dimethylphenol in 21% overall yield. Reaction of **1** with $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ gave the unexpectedly stable hydroquinone-containing binuclear Cu(II) complex [2,6-bis[*N*-2-(2'-pyridylethyl)formimidoyl]-4-hydroxy-1-phenolato]biscopper(II) bisperchlorate (**8**). The crystal and molecular structure of **8** was determined by X-ray analysis. The complex crystallizes in the triclinic space group $P\bar{1}$, with $Z = 2$ in a unit cell of the following dimensions: $a = 9.399$ (2) Å, $b = 10.469$ (1) Å, $c = 14.612$ (4) Å, $\alpha = 102.72$ (2)°, $\beta = 100.71$ (2)°, $\gamma = 104.60$ (2)°. Surprisingly high reactivity of **8** was observed in catalytic oxidations of hydroquinones and α-hydroxy ketones using molecular oxygen as the oxidant. A mechanistic discussion is provided.

Currently much effort is devoted to develop useful catalytic systems for mild and selective oxidations with the aid of molecular oxygen.[1] Furthermore it is of great interest to elucidate the factors that determine the (reversible) binding and activation of O_2 in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity.[2] Guided by nature, intriguing model systems[3] for copper-containing enzymes such as hemocyanin[2,4] have been developed. Considerable progress has been made in order to establish the active species in cytochrome P450 and related oxygenases.[5] Contrary to the successful development of oxidation catalysts based on metalloporphyrins,[6] synthetically useful catalysts based on copper complexes that act as mimics for copper-containing monooxygenases (e.g. tyrosinase

Scheme I



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and dopamine-β-hydroxylase[7,8]) have hardly been found. This is even more surprising if one realizes that selective oxidations of organic substrates mediated by copper–amine complexes have been known for over a century.[1,9-11] The Glaser oxidative coupling of acetylenes,[11] the oxidative dimerization of naphthols as observed by Havinga and Brackman,[12] and the formation of poly(phenylene ethers) from 2,6-disubstituted phenols as discovered by Hay[13] are all based on copper–amine complexes and molecular oxygen. Numerous studies have dealt with these oxidations,[10] and useful extensions to γ-oxidation of enones,[14] asymmetric phenol oxidations,[15] and *cis,cis*-muconic acid synthesis[16] as well as improvements on poly(1,4-phenylene ether) formation have been found.[10,17] Stoichiometric arene hydroxylation has been observed[18,19] during studies of the reactivity of O_2 at copper centers in binuclear complexes designed to mimic certain oxygenases. Furthermore, catalytic dehydrogenations[19,20] and phosphine and sulfide oxidations[21] were reported.

As part of our continuing efforts to develop *bimetallic complexes* that can act as catalysts for selective oxidation[19,22] using molecular oxygen, we describe here novel model systems.

The effect of a "second metal" in the catalyst complex is proposed to enhance the oxygen binding ability, to assist in oxygen–oxygen bond cleavage, or to interfere with substrate binding.

Two approaches for the successful development of a selective oxidation catalyst can be followed: (i) One oxygen atom of O_2 is incorporated into the substrate,[1,23] as in tyrosinases. These monooxygenases,[2,24] with two copper ions in the active center, catalyze the incorporation of one oxygen atom into the ortho position of phenols; an external electron and proton source is required to convert the second oxygen atom into water. In cytochrome P450 based metalloporphyrin catalysts,[5,6] this problem is circumvented either by the use of "single-oxygen" donors[6,25] or by the use of an external reducing agent.[6,26] (ii) Both oxygen atoms of O_2 are used for substrate oxidation as is the case with dioxygenases.[1,23] Groves and Quinn[27] have devised an elegant system for oxygen–oxygen bond fission and aerobic epoxidation based on sterically hindered ruthenium porphyrins. In the approach described in this paper, a copper(I)–copper(II) redox couple and a hydroquinone–quinone redox couple are incorporated in one catalytically active complex, as is shown in Scheme I.

It is intended to activate molecular oxygen, either as superoxo or μ-peroxo, via electron transfer from the Cu(I) binuclear system. The hydroquinone–quinone moiety acts in this system as an electron shunt between an external reducing agent and the copper ions. This mechanism of electron transfer is reminiscent of the quinone-based electron-transfer systems as found for instance in the bacterial photosynthetic system[28] and in synthetic metalloporphyrin–quinone electron-transfer systems.[29]

Experimental Section

All experiments with hydroquinones were performed under an inert (N_2) atmosphere. For the oxidation experiments, pure oxygen (Air Products) was used. Oxygen uptake was measured by using manometric techniques. Tetrahydrofuran was distilled from sodium benzophenone ketal under a N_2 atmosphere. All other solvents were distilled before use. 2,6-Xylenol (Janssen) were used as such. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.48 MHz) spectra were obtained on a Varian VXR 300 spectrometer. Chemical shifts are reported as δ values relative to tetramethylsilane (δ = 0 ppm). Infrared spectra were recorded on a Unicam SP 200 infrared spectrophotometer. Melting points (uncorrected) were determined on a Mettler FP-2 melting point apparatus. High-resolution mass spectra (HRMS) were recorded on a AEI-MS-902 spectrometer. Elemental analysis were performed in the microanalytical department of this laboratory.

2,6-Dimethyl-1,4-hydroquinone (3). To a solution of 60 g of KH_2PO_4 in 700 mL of H_2O was added 10 g (82 mmol) of 2,6-xylenol dissolved in 200 mL of methanol. Freshly prepared Fremi's salt[30] (60 g, 112 mmol) was subsequently added in two portions to the well-stirred mixture prepared above. Stirring was continued for 1 h at room temperature, and the resulting reaction mixture was extracted with diethyl ether (3 × 50 mL). The organic extracts were dried over $MgSO_4$, the solvent was removed in vacuo, and the solid residue was purified by crystallization from petroleum ether (60–80 °C) to give 8.0 g (75%) of yellow crystalline **3**; mp 74–75 °C (lit.[31] mp 73–75 °C).

A solution of 5.0 g (37 mmol) of 2,6-dimethylquinone in $CHCl_3$ (100 mL) was vigorously shaken for 10 min with a solution of $Na_2S_2O_4$ (10 g) in aqueous NaOH (8.0 g of NaOH in 100 mL of H_2O). The aqueous layer was separated, acidified (aqueous HCl), and extracted with $CHCl_3$ (2 × 50 mL). The combined chloroform solutions were dried over $MgSO_4$, and the solvent was removed by rotatory evaporation to yield a white solid. Crystallization from H_2O gave 4.1 g (81%) of **3**; mp 149–151 °C (lit.[32] mp 151–152 °C).

2,6-Dimethyl-1,4-hydroquinone 1,4-Dibenzoate (4). To a solution of 4.0 g (29 mmol) of 2,6-dimethylhydroquinone (**3**) and 5.9 g (58 mmol) of triethylamine in 200 mL of CH_2Cl_2 was added, at room temperature over a period of 1 h, 8.2 g (58 mmol) of benzoyl chloride. The resulting mixture was stirred for an additional 1 h and subsequently poured into 100 mL of H_2O. The CH_2Cl_2 layer was separated and washed with 2 N aqueous HCl (twice), aqueous 10% NaOH solution, and brine. After drying over $MgSO_4$ and removal of the solvent by rotary evaporation, the solid residue was crystallized from petroleum ether (60–80 °C). There was obtained 8.3 g (85%) of pure **4** as white needles: mp 117.5–118.4 °C; ^{1}H NMR ($CDCl_3$) 2.23 (s, 6 H), 6.97 (s, 2 H), 7.37–7.73 (m, 6 H), 8.08–8.37 (m, 4 H); ^{13}C NMR ($CDCl_3$) 16.44 (q), 121.34 (d), 128.42 (d), 128.53 (d), 128.99 (s), 129.43 (s), 130.03 (d), 131.64 (s), 133.41 (d), 133.54 (d), 145.77 (s), 148.02 (s), 164.11 (s), 165.05 (s). Mass spectrum (EI, M^+): calcd m/e 346.120, found m/e 346.119. Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.42; H, 5.32. Found: C, 76.30; H, 5.32.

2,6-Bis(dibromomethyl)-1,4-hydroquinone 1,4-Dibenzoate (5). To a stirred solution of 7.0 g (20.2 mmol) of **4** in 150 mL of CCl_4, heated at

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reflux and continuously irradiated with an IR photolamp, was slowly added over a 1-h period 13.0 g (81 mmol) of bromine. After the addition was complete, the resulting mixture was heated and irradiated for an additional period of 12 h. By that time the bromine had completely disappeared. The solvent was removed by distillation and the residue purified by crystallization from petroleum ether (60–80 °C), affording **5** as white crystalline material: yield 11.2 g (83%); mp 177.5–179.7 °C; ^{1}H NMR ($CDCl_3$) 6.57 (s, 2 H), 7.33–7.76 (m, 6 H), 7.83 (s, 2 H), 8.03–8.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) 32.17 (d), 125.20 (d), 127.40 (s), 128.70 (d), 129.07 (d), 130.28 (d), 130.44 (s), 130.75 (d), 134.04 (d), 134.77 (d), 135.87 (d), 137.33 (s), 149.25 (s), 163.55 (s), 164.22 (s). Mass spectrum (EI, M^+): calcd m/e 657.761, found m/e 657.763. Anal. Calcd for $C_{22}H_{14}Br_4O_4$: C, 39.88; H, 2.11; Br, 48.34. Found: C, 39.55; H, 2.11; Br, 48.70.

1,4-Hydroquinone-2,6-dicarboxaldehyde (6). A solution of 5.0 g (7.3 mmol) of **5** in 50 mL of concentrated H_2SO_4 was stirred at room temperature for 16 h. The solution was slowly poured onto 150 g of crushed ice, and the aqueous mixture was subsequently extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (3 × 30 mL of a 1 N solution) and dried over $MgSO_4$, and the solvent was removed in vacuo. Crystallization of the yellow residue from H_2O gave the title compound **6**: yellow solid, 0.45 g (40%); mp 170–174 °C; ^{1}H NMR (NaOD, D_2O) 7.30 (s, 2 H), 10.15 (s, 2 H); ^{13}C NMR (D_2O, NaOD, CD_3OD) 118.86 (d), 120.05 (s), 145.29 (s), 163.17 (s), 185.42 (d). Mass spectrum (EI, M^+): calcd m/e 166.027, found m/e 166.028.

2,6-Bis[*N*-2-(2′-pyridylethyl)formimidoyl]-1,4-dihydroxybenzene (1). To a stirred solution of 0.10 g (0.6 mmol) of **6** in 50 mL of CH_2Cl_2 was added 0.147 g (1.2 mmol) of 2-(2′-pyridyl)ethylamine. The mixture was stirred at room temperature for 1 h, and subsequently 1.0 g of Na_2SO_4 was added. After being stirred for an additional 1 h, the solution was filtered and evaporated to dryness to afford **1** as a red-brown oil, yield 0.21 g (93%), which was homogeneous by ^{1}H NMR spectroscopy: ^{1}H NMR ($CDCl_3$) 3.15 (t, 4 H), 3.95 (t, 4 H), 7.0–7.3 (m, 6 H), 8.40 (s, 2 H), 8.55 (d, 2 H), 9.82 (s, 2 H); ^{13}C NMR ($CDCl_3$) 38.99 (t), 59.16 (t), 119.71 (d), 121.11 (s), 121.44 (d), 123.62 (d), 136.49 (d), 148.65 (s), 148.86 (d), 155.64 (s), 158.92 (s), 161.62 (d). Mass spectrum (EI; M^+): calcd m/e 374.174, found m/e 374.173.

[2,6-Bis[*N*-2-(2′-pyridylethyl)formimidoyl]-4-hydroxy-1-phenolato]-biscopper(II) Bisperchlorate (8). Sodium hydride (0.027 g, 1.13 mmol) was suspended in THF (30 mL) and treated with 0.21 g (0.56 mmol) of **1** dissolved in THF (10 mL). The resulting solution was stirred and heated at reflux for 1 h. The solvent was removed in vacuo, and the yellow disodium salt **7** was dissolved in absolute ethanol (20 mL) and added to a solution of 0.42 g (1.13 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in absolute ethanol (10 mL). The resulting mixture was heated at reflux for 2 h and subsequently concentrated in vacuo. The solid residue was crystallized from $MeOH/H_2O$ to afford dark-green crystalline **8**: yield 0.143 g (36%); IR (KBr, cm^{-1}) 3500 (br, OH), 1650, 1615, 1580, 1100 (CBr str), 850, 780. Anal. Calcd for $C_{22}H_{22}Cl_2Cu_2N_4O_{11}$: C, 36.87; H, 3.07; N, 7.82. Found: C, 36.79; H, 3.28; N, 7.77.

X-ray Diffraction: Crystal and Molecular Structure of 8. A suitable green plate-shaped crystal, cleaved from an intergrown specimen obtained by recrystallization from $MeOH/H_2O$, was glued on the top of a glass fiber and transferred to the Enraf-Nonius CAD-4F diffractometer. Unit cell dimensions and their standard deviations were determined from the setting angles of 22 reflections in the range $10.15° < \theta < 11.88°$ in four alternate settings. The unit cell was identified as triclinic, space group $P\bar{1}$. Reduced cell calculations did not indicate any higher lattice symmetry. This choice was confirmed by the solution and the successful refinement of the structure. Two standard reflections were monitored at regular intervals and showed negligible change during the data collection period. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects. The correction for absorption was judged to be not necessary in view of the observed small intensity variation, up to 8%, for an 360° ψ scan of the close-to-axial reflection (132). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance[33] of the three reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.014I)^2$ resulting in 2101 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. Pertinent numerical data on the structure determination are summarized in Table I and in the supplementary material. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86[34]); it was completed by Fourier techniques. Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of 18 hydrogen atoms; the remaining four hydrogen atoms (H(14), H(82), H(92), and H(172)) were introduced at calculated positions (C–H = 1.0 Å). Thereby the found H atoms served to determine the conformation. Due to the low observation to parameter ratio in the final calculation, hydrogen atoms were refined in the riding mode and with one common temperature factor. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one overall isotropic temperature factor for the hydrogen atoms converged at $R_F = 0.050$ ($R_w = 0.050$). High thermal motion, but no resolvable disorder, was sited for the C(8) atom. A final difference Fourier map did not show unusual features. The details of the final refinements are summarized below. The final values of the refined positional parameters, fraction atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms, and molecular geometry data are collected in Tables II and III and as supplementary material. Tables of hydrogen atom positions, thermal parameters, comprehensive bond distances and angles, and F_o, F_c, and $\sigma(F)$ values are given as supplementary material for this paper.

All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL and EUCLID (calculation of geometric data) and a locally modified version of the program PLUTO.[35]

Table I. Crystal Data and Details of the Structure Determination

chem formula	$C_{22}H_{22}Cu_2N_4O_3(ClO_4)_2$
mol wt	716.43
cryst system	triclinic
space group, No.	$P\bar{1}$, 2
a, Å	9.399 (2)
b, Å	10.469 (1)
c, Å	14.612 (4)
α, deg	102.72 (2)
β, deg	100.71 (2)
γ, deg	104.60 (2)
V, Å^3	1312.1 (5)
Z	2
D_{calc}, g·cm^{-3}	1.813
$F(000)$, electrons	724
μ(Mo K$\bar{\alpha}$), cm^{-1}	19.0
approx cryst dimens, mm	0.15 × 0.15 × 0.07

Catalytic Oxidations with 8. Typical Procedure: Oxidation of Benzoin. Benzoin (**15**, 0.183 g, 0.86 mmol) and **8** (0.010 g, 0.01 mmol) were dissolved in 10 mL of methanol in a 100-mL three-necked bottle. The reaction vessel was put in a thermostated bath maintained at 19 °C and connected to a gas buret filled with dioxygen. The mixture was equilibrated for 30 min. Subsequently, 0.040 g (1.0 mmol) of NaOH dissolved in 1 mL of methanol was added at once. The reaction mixture was vigorously shaken and the oxygen uptake measured.

After 2 min oxygen uptake declined; after 5 min, it stopped completely, resulting in a total O_2 consumption of 20.5 ± 1 mL (0.85 ± 0.05 mmol). The methanolic solution was acidified with aqueous HCl, and most of the MeOH was evaporated. The resulting aqueous layer was extracted three times with 10 mL of diethyl ether.

The combined ether layers were dried over $MgSO_4$ and evaporated to dryness. The white solid was crystallized from petroleum ether (40–60°C). Benzil (0.178 g, 98%), identical in all respects with an independent sample, was obtained. Traces of benzaldehyde (approximately 1%) were found. If 0.009 g (0.23 mmol) of NaOH was used instead of stoichiometric amounts of base, the oxygen uptake stopped after 5.8 ± 0.5 mL (0.24 ± 0.03 mmol) of O_2 had been consumed.

The oxidation of hydroquinone was performed by following the typical procedure described above. The product was identical in all respects with an independently prepared sample; however, only small amounts of product could be isolated because of the instability of the quinone under the specific reaction conditions.

Results and Discussion

Ligand Synthesis. With the purpose of designing binuclear copper complexes in which a hydroquinone (or quinone) moiety

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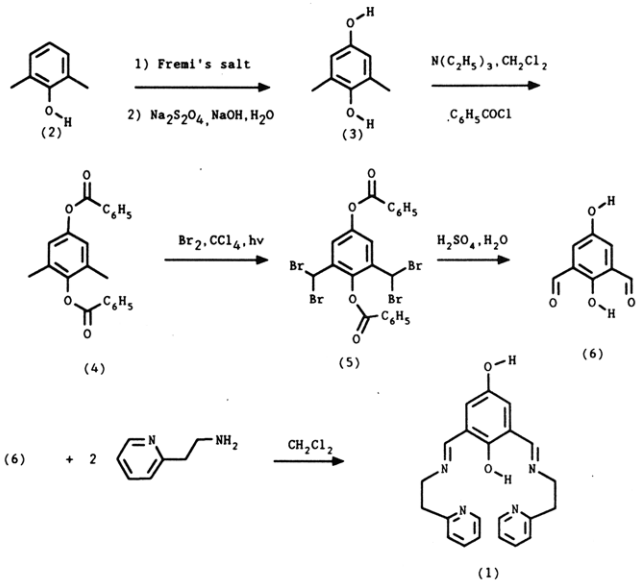
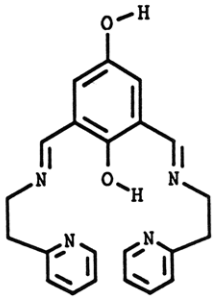
Scheme II



is incorporated, the new ligand 1,3-bis[*N*-2-(2′-pyridylethyl)-formimidoyl]-2,5-dihydroxybenzene (**1**) was synthesized. The



(1)

synthesis of ligand **1** is outlined in Scheme II. Oxidation of 2,6-dimethylphenol with Fremi's salt[30] followed by a reduction of 2,6-dimethylquinone to 2,6-dimethylhydroquinone using sodium dithionite and subsequent protection of the phenolic groups by dibenzoylation afforded **4** in 64% overall yield as crystalline material. Careful radical bromination of **4** with a 2-fold excess of bromine under continuous irradiation[36] gave pure tetrabromo derivative **5** in 83% yield. The formation of **5** can also be achieved using *N*-bromosuccinimide. Bromination of the aryl groups, a notorious side reaction under certain conditions, was not observed, and mono- or tribromo-substituted analogues of **5** were not obtained. The fact that dibromo substitution has taken place at each methyl substituent in **4** can also readily be deduced from the singlet observed at 6.60 ppm for the allylic hydrogen of **5** in the ^1H NMR spectrum. Exhaustive hydrolysis of **5** in sulfuric acid removes both protective groups and liberates both aldehyde functionalities. Only limited use has been made of the conversion of xylenes into phthalic dialdehydes using the tetrabromination–hydrolysis sequence. The formation of isophthalic aldehyde from *m*-xylene has been reported.[37] In our hands this proved to be an excellent procedure to prepare various isophthalic aldehydes. Hydroquinone **6** has a simple ^1H NMR spectrum in D_2O/NaOD with singlets at 7.30 and 10.15 ppm for the aryl and aldehyde hydrogens, respectively. As expected, compound **6** is rather prone to oxidative decomposition but can be stored well under nitrogen in the cold. Condensation of **6** with 2 equiv of 2-(2′-pyridyl)ethylamine in CH_2Cl_2 afforded **1** in high yield, sufficiently pure (as determined by ^1H NMR spectroscopy) for the preparation of metal complexes.

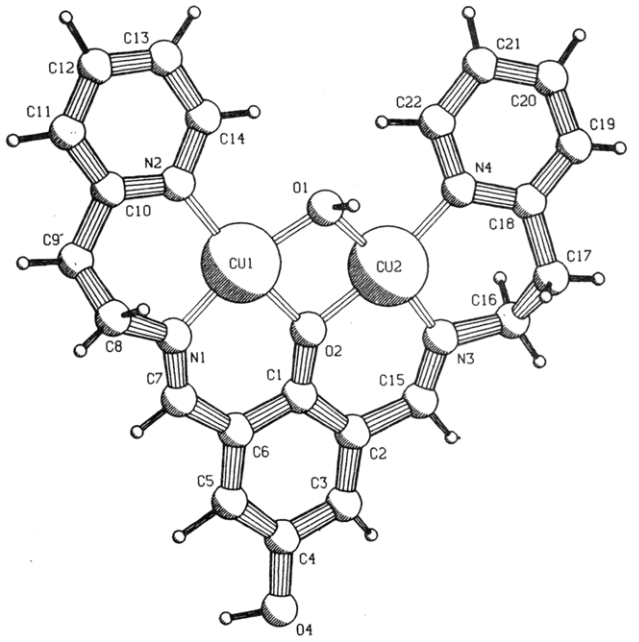
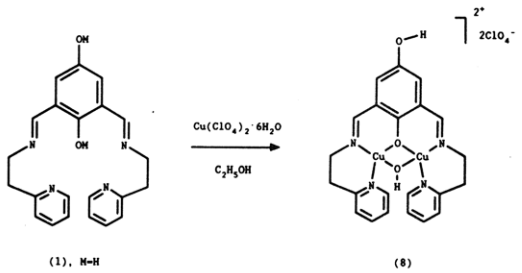


Figure 1. ORTEP plot of the X-ray structure of complex **8**.

Table II. Selected Bond Distances (Å)

Cu(1)–Cu(2)	2.991 (2)	N(4)–C(18)	1.35 (1)
Cu(1)–O(1)	1.922 (7)	N(4)–C(22)	1.34 (1)
Cu(1)–O(2)	1.971 (6)	C(1)–C(2)	1.41 (1)
Cu(1)–O(5)	2.481 (9)	C(1)–C(6)	1.42 (1)
Cu(1)–N(1)	1.92 (1)	C(2)–C(15)	1.46 (1)
Cu(1)–N(2)	2.014 (7)	C(2)–C(3)	1.40 (1)
Cu(2)–O(1)	1.928 (7)	C(3)–C(4)	1.38 (1)
Cu(2)–O(2)	1.955 (7)	C(4)–C(5)	1.37 (1)
Cu(2)–O(6)	2.59 (1)	C(5)–C(6)	1.39 (1)
Cu(2)–N(3)	1.939 (9)	C(6)–C(7)	1.44 (1)
Cu(2)–N(4)	2.004 (8)	C(8)–C(9)	1.34 (1)
Cl(1)–O(5)	1.408 (9)	C(9)–C(10)	1.49 (1)
Cl(1)–O(6)	1.39 (1)	C(10)–C(11)	1.39 (1)
Cl(1)–O(7)	1.36 (1)	C(11)–C(12)	1.35 (1)
Cl(1)–O(8)	1.39 (1)	C(12)–C(13)	1.35 (1)
O(2)–C(1)	1.32 (1)	C(13)–C(14)	1.38 (1)
O(4)–C(4)	1.38 (1)	C(16)–C(17)	1.51 (1)
N(1)–C(7)	1.27 (1)	C(17)–C(18)	1.51 (1)
N(1)–C(8)	1.48 (2)	C(18)–C(19)	1.38 (1)
N(2)–C(10)	1.34 (1)	C(19)–C(20)	1.36 (1)
N(2)–C(14)	1.35 (1)	C(20)–C(21)	1.36 (1)
N(3)–C(15)	1.28 (1)	C(21)–C(22)	1.37 (1)
N(3)–C(16)	1.48 (1)		

Synthesis and Crystal and Molecular Structure of Binuclear Cu(II) Complex 8. The ligand **1** was doubly deprotonated with NaH in tetrahydrofuran to afford the bissodium salt **7**. Subsequently it reacted with 2 equiv of copper(II) perchlorate hexahydrate in ethanol (eq 1). After recrystallization from aqueous



(1)

ethanol there was obtained the dark green binuclear Cu(II) complex **8** in 36% yield. As elemental analysis and spectroscopic data did not provide conclusive evidence for the presence of a quinone- or a hydroquinone-containing copper(II) complex, a molecular structure determination was undertaken.

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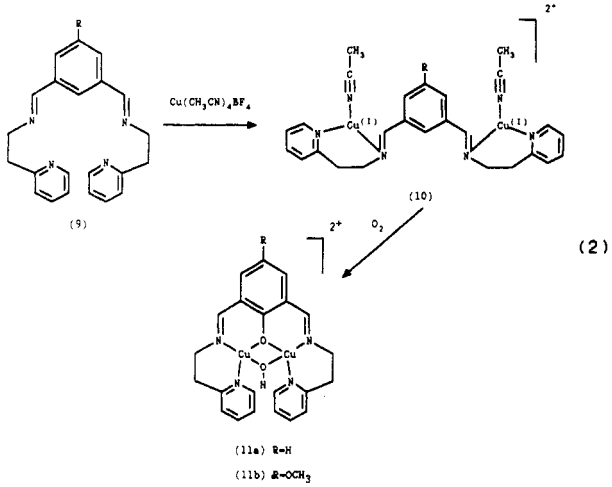
Table III. Selected Bond Angles (deg)

Cu(2)-Cu(1)-O(1)	39.1 (1)	C(7)-N(1)-C(8)	119 (1)
Cu(2)-Cu(1)-O(2)	40.2 (1)	Cu(1)-N(2)-C(10)	124.9 (7)
Cu(2)-Cu(1)-O(5)	83.3 (1)	Cu(1)-N(2)-C(14)	117.4 (7)
Cu(2)-Cu(1)-N(1)	131.4 (3)	C(10)-N(2)-C(14)	117.3 (8)
Cu(2)-Cu(1)-N(2)	132.5 (2)	Cu(2)-N(3)-C(15)	125.4 (7)
O(1)-Cu(1)-O(2)	78.6 (3)	Cu(2)-N(3)-C(16)	118.7 (6)
O(1)-Cu(1)-O(5)	93.7 (3)	C(15)-N(3)-C(16)	115.9 (9)
O(1)-Cu(1)-N(1)	164.2 (3)	Cu(2)-N(4)-C(18)	123.1 (6)
O(1)-Cu(1)-N(2)	95.8 (3)	Cu(2)-N(4)-C(22)	117.8 (7)
O(2)-Cu(1)-O(5)	85.0 (3)	C(18)-N(4)-C(22)	119.1 (8)
O(2)-Cu(1)-N(1)	91.3 (3)	O(2)-C(1)-C(2)	121.8 (8)
O(2)-Cu(1)-N(2)	169.8 (3)	O(2)-C(1)-C(6)	120.1 (8)
O(5)-Cu(1)-N(1)	97.5 (4)	C(2)-C(1)-C(6)	118.0 (8)
O(5)-Cu(1)-N(2)	86.8 (3)	C(1)-C(2)-C(15)	122.3 (8)
N(1)-Cu(1)-N(2)	95.9 (4)	C(1)-C(2)-C(3)	120.1 (9)
Cu(1)-Cu(2)-O(1)	39.0 (1)	C(15)-C(2)-C(3)	117.6 (9)
Cu(1)-Cu(2)-O(2)	40.6 (1)	C(2)-C(3)-C(4)	121.1 (9)
Cu(1)-Cu(2)-O(6)	81.4 (2)	C(3)-C(4)-O(4)	117.3 (9)
Cu(1)-Cu(2)-N(3)	132.1 (2)	C(3)-C(4)-C(5)	119.5 (9)
Cu(1)-Cu(2)-N(4)	131.0 (2)	O(4)-C(4)-C(5)	123 (1)
O(1)-Cu(2)-O(2)	78.8 (3)	C(4)-C(5)-C(6)	122 (1)
O(1)-Cu(2)-O(6)	90.6 (3)	C(1)-C(6)-C(5)	119.5 (9)
O(1)-Cu(2)-N(3)	170.3 (3)	C(1)-C(6)-C(7)	122.8 (8)
O(1)-Cu(2)-N(4)	93.2 (3)	C(5)-C(6)-C(7)	117.4 (9)
O(2)-Cu(2)-O(6)	85.3 (3)	N(1)-C(7)-C(6)	129 (1)
O(2)-Cu(2)-N(3)	91.8 (3)	N(1)-C(8)-C(9)	117 (2)
O(2)-Cu(2)-N(4)	171.4 (3)	C(8)-C(9)-C(10)	120 (1)
O(6)-Cu(2)-N(3)	91.0 (3)	N(2)-C(10)-C(9)	120 (1)
O(6)-Cu(2)-N(4)	91.8 (3)	N(2)-C(10)-C(11)	122 (1)
N(3)-Cu(2)-N(4)	96.3 (3)	C(9)-C(10)-C(11)	118 (1)
O(5)-Cl(1)-O(6)	112.3 (6)	C(10)-C(11)-C(12)	119 (1)
O(5)-Cl(1)-O(7)	112.3 (6)	C(11)-C(12)-C(13)	120 (1)
O(5)-Cl(1)-O(8)	108.1 (7)	C(12)-C(13)-C(14)	118 (1)
O(6)-Cl(1)-O(7)	110.8 (7)	N(2)-C(14)-C(13)	123 (1)
O(6)-Cl(1)-O(8)	104.5 (7)	N(3)-C(15)-C(2)	128.5 (9)
O(7)-Cl(1)-O(8)	108.5 (8)	N(3)-C(16)-C(17)	111.2 (9)
Cu(1)-O(1)-Cu(2)	101.9 (3)	C(16)-C(17)-C(18)	113.6 (9)
Cu(1)-O(2)-Cu(2)	99.2 (3)	N(4)-C(18)-C(17)	117.2 (9)
Cu(1)-O(2)-C(1)	130.0 (6)	N(4)-C(18)-C(19)	119.6 (9)
Cu(2)-O(2)-C(1)	130.1 (6)	C(17)-C(18)-C(19)	123 (1)
Cu(1)-O(5)-Cl(1)	131.2 (5)	C(18)-C(19)-C(20)	120 (1)
Cu(2)-O(6)-Cl(1)	128.0 (6)	C(19)-C(20)-C(21)	120 (1)
Cu(1)-N(1)-C(7)	125.5 (8)	C(20)-C(21)-C(22)	118 (1)
Cu(1)-N(1)-C(8)	115.3 (8)	N(4)-C(22)-C(21)	123 (1)

The crystal structure of **8** was determined by a single-crystal X-ray diffraction study. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. An ORTEP drawing of the molecule, with the adopted numbering scheme and illustrating the puckering, is shown in Figure 1. Each asymmetric unit contains one complete molecule of the title compound and two perchlorate residues. Crystal data and details of the structure determination are shown in Table I. Tables II and III contain selected bond distances and angles, respectively (see also Experimental Section). The X-ray analysis shows that the molecule is a unique biscopper(II)-hydroquinone complex. In contrast to expectation,[38] the hydroquinone moiety was not oxidized to a quinone in the presence of the two copper(II) ions in the complex. Both copper ions are coordinated to a bidentate (pyridylethyl)imine ligand and are bridged by a phenolate and a hydroxy group, adopting a slightly disorted square-planar geometry. The molecular structure of **8** shows strong similarities with that of the *p*-hydroxy analogue **11a**, which was obtained by oxygen insertion into the *C*(1)(aryl) hydrogen bond of the corresponding binuclear Cu(I) complex **10**, derived from ligand **9** (eq 2).[19] The Cu(I)-Cu(II) bond distances of **8** (2.991 (2) Å) and **11a** (2.990 (2) Å)[19] are equal and typical of binuclear copper complexes containing two, one-atom bridging ligands.[39] The four-membered Cu_2O_2 unit deviates from planarity with a O(1)-Cu(1)-O(2)-Cu(2) torsion angle of −9.3 (3)°. The C(1)-O(2) bond (bond distance 1.32 (1) Å) in **8** is shorter than the C(4)-O(4) bond (bond distance 1.38 (1) Å) but is slightly longer than the phenolate C-O bond in **11a** (bond distance 1.309 (7) Å). The C-O bond distances are substantially longer than those in free quinones[40] (1.208 Å), in a Ni(II)-coordinated quinone[41] (1,23 Å), or the average value of 1.27 Å found for the C-O bond length in a semiquinone coordinated to Ni(II).[41] Combining these data with the results of the refinement using anisotropic thermal parameters, which provided the location of the hydrogen atoms at O(4), leads to the conclusion that the phenolic moiety is present as the Cu(II)-bridged hydroquinone structure. A semiquinone structure, as has been observed for nickel(II)[42] and copper(II) catecholate complexes,[43] is unlikely on the basis of the data provided and the similar Cu-O distances found in **8** and **11a** (see Table II and ref 19). The findings described here contrast with the formation of a quinone-semiquinone adduct of $Ni^{II}(ClO_4)_2$ with tetrachlorocatechol.[41] An extensive coordination chemistry of catecholates and semiquinones with group VIII transition metals has been developed,[44] since transition-metal quinoid adducts provide interesting perspectives as redox catalysts, in biological applications, and in the formation of conducting systems. Although the hydroquinone in **8** is ideally situated for electron transfer toward copper ions, this does not readily take place even in the presence of molecular oxygen. It has been suggested for related Ni complexes[41] that despite the fact that the metal ion acts as an electron sink, back-donation of electrons toward a coordinated quinone might take place, depending strongly upon the redox potentials of quinone and metal and the levels of π orbitals and metal d orbitals. Electron paramagnetic resonance spectroscopy (EPR) measurements between room temperature and −130 K of binuclear Cu(II) complex **8** dissolved in dimethyl sulfoxide showed that complex **8** is EPR silent in this temperature range.[45]

Finally, we have recently prepared the biscopper(II) complex **11b**, which contains a hydroquinone monoether ligand, in contrast to **8** containing the hydroquinone ligand system.[46] The complex **11b** was obtained from the corresponding binuclear Cu(I) complex **12** via a hydroxylation-induced demethoxylation with the aid of molecular oxygen (eq 3). There are no indications that either



(2)

(38) *Oxidative Coupling of Phenols*; Taylor, W. I., Battersby, A. R.; Eds.; Marcel Dekker Inc.: New York, 1967. Feringa, B. L. Thesis, University of Groningen, 1978.
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(41) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *J. Am. Chem. Soc.* **1988**, *110*, 6897.
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(46) Gelling, O. J.; Bolhuis, F. van; Feringa, B. L. *J. Am. Chem. Soc.*, in press.

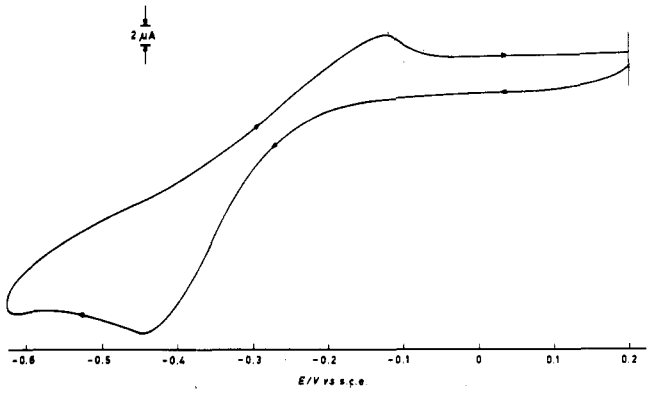
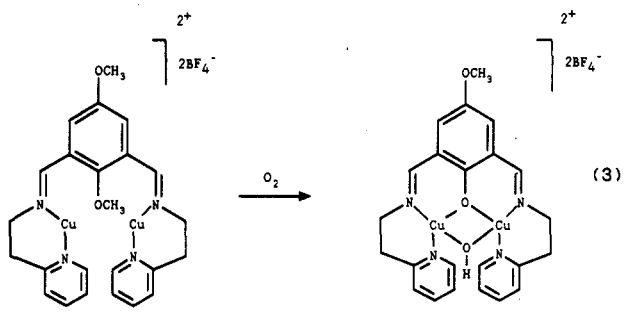
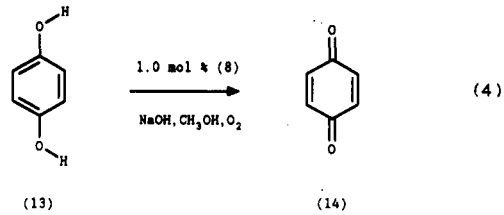


Figure 2. Cyclic voltammogram of complex **8** in acetonitrile (30-s dip; SCE and Pt electrodes, 50 mV/s).

quinone or semiquinone complexes are formed during the oxidation of **12**.



Catalytic Oxidations. As was described above, no oxidation of the hydroquinone moiety in **1** takes place by using cupric ions and molecular oxygen. Much to our surprise, the binuclear Cu(II) complex **8**, derived from **1**, acts as a catalyst for the oxidation of hydroquinone to quinone using molecular oxygen as the oxidant (eq 4). Thus, in the presence of catalytic amounts (1 mol %)

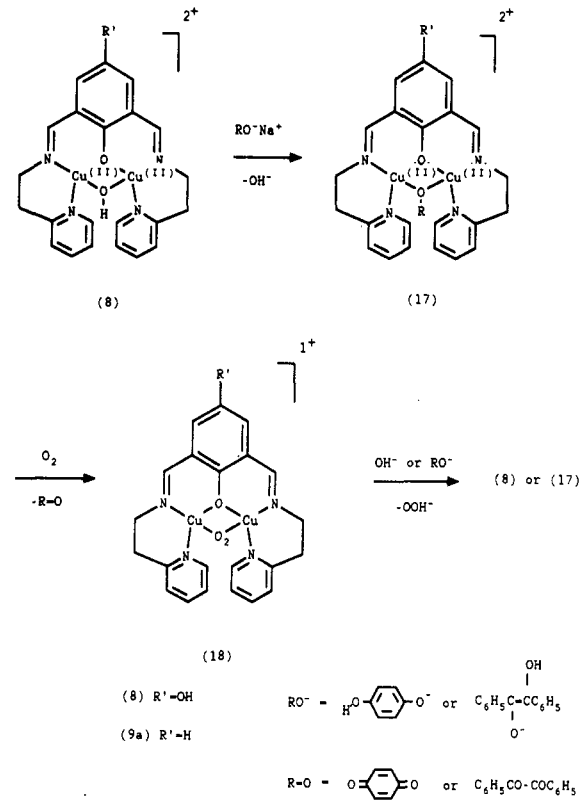


of **8**, hydroquinone (**13**) is completely converted into **14** under aerobic conditions.

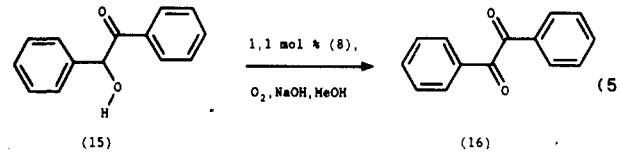
Apparently the two electron-withdrawing imine substituents present in ligand **1** sufficiently increase the oxidation potential of the hydroquinone moiety to prevent intramolecular electron transfer to the Cu(II) ions in **8**. However, fast intermolecular electron transfer from **13** to complex **8** can apparently take place. Cyclic voltammetric studies with complex **8** under different conditions using dipping methods showed no reversible oxidation–reduction patterns. In acetonitrile as the solvent, only one reduction peak was seen at −0.47 V versus SCE (standard calomel electrode) and a small oxidation peak was seen at −0.12 V versus SCE. In the subsequent runs, the current decreases gradually. Presumably an irreversible reduction of the sensitive imine bonds of **8** takes place. A typical example of a cyclic voltammetric measurement with **8** is given in Figure 2.

Hydrogen peroxide was not detected as the two-electron reduction product from O_2 during these oxidations. Furthermore, we have not obtained any indication for the involvement of the hydroquinone moiety in **8** during the catalytic oxidation, other than acting as a bridging ligand between the two Cu(II) ions. Thus, **8** was recovered unchanged after the oxidation as shown by UV spectra and via liberation of the ligand using Karlin's

Scheme III



method.[47] This is in accordance with the observed stability of **8** under aerobic conditions. In addition, we have recently observed that **11a** is capable of using molecular oxygen to oxidize phenols and hydroquinones without affecting the ligand.[19,48] Since oxidation of the hydroquinone to quinone moiety in **8** does not take place to form the corresponding biscopper(I) complex, the activation of O_2 is prohibited and complex **8** is not active as a catalyst for oxygenation reactions. To obtain further evidence for the ability of **8** to act as a dehydrogenation catalyst, the conversion of α-hydroxy ketones was examined. In a typical example benzoin is converted into benzil (eq 5). A rapid dehydrogenation takes



place under basic conditions and a turnover of 1032/h (based on catalyst) was reached. As base is essential for this oxidation reaction to occur, it proved to be possible to control the oxidation of **15** by the rate of addition of base. The results show a stoichiometric reaction with respect to NaOH, O_2, and benzoin.

A mechanistic rational for the catalytic dehydrogenation mediated by **8**, in accordance with the data obtained, is given in Scheme III. Extensive mechanistic studies will be necessary to substantiate this scheme. Binding of the substrate to one or two copper ions as in **17** is followed by a two-electron transfer to yield a binuclear Cu(I) complex. Subsequent binding of molecular oxygen is thought to result in the formation of peroxy complex **18**. Similar binding of phenolate anions followed by O_2 binding to binuclear Cu(II) complexes has been proposed as the first step in the catalytic oxidative polymerization of 2,6-dimethylphenol.[49] Substantial evidence for the formation of peroxodicopper(II)

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complexes from phenoxo-bridged dicopper(I) complexes has been reported by Karlin and co-workers.[50] Furthermore, a recent crystal structure of a (μ-1,2-peroxo)dicopper(II) complex without a bridging ligand between the two copper centers has been reported.[51]

As the addition of base is essential for the oxidation to occur, we speculate that the role of the base is to deprotonate the substrate (ROH) either before or after binding to one or two copper ions in the binuclear complex. This is in line with mechanistic proposals in oxidative phenol coupling.[49,52] Alternative mechanisms as the one shown in Scheme III might be proposed; for instance, the redox reaction of complex **18** with deprotonated substrate is an attractive possibility. This points to a reversal of the sequence, as shown in Scheme III. It should be emphasized that 1 mol of O_2/mol of substrate is consumed, indicating a two-electron-transfer process contrary to four-electron-transfer processes that lead ultimately to H_2O as was observed in copper(II)-mediated oxidative phenol coupling.[49] In situ (catalytic) decomposition of hydroperoxide anion cannot be excluded. In a control experiment adding 30% H_2O_2 to a methanolic solution of **8** and NaOH, we were not able to detect peroxide after 1 h at room temperature, indicating H_2O_2 decomposition.

The presence of a hydroquinone or phenol moiety in the aforementioned ligands is only essential for bridging in the Cu(II) ions, but has, as far as was observed experimentally, no role in the redox process. Furthermore, it can be concluded that the intended application of the hydroquinone moiety as an electron shunt between an external reducing agent and the Cu(II) ions (and thus molecular oxygen) is not possible with the present model system. Appropriate modifications of ligand **1** and complexes derived thereof that fulfill the requirements mentioned above might be obtained by reduction of the imine functionalities. It is expected that this will result in a lowering of the oxidation potential of the hydroquinone moiety.

In conclusion we have reported here the synthesis of a new ligand system **1** containing a hydroquinone moiety capable of forming binuclear complexes. The molecular structure of an unprecedented, stable, binuclear hydroquinone-containing Cu(II) complex **8** was determined. Furthermore, efficient catalytic dehydrogenations of hydroquinone and α-hydroxy ketones using O_2 were found. However, no oxygenation (O-transfer) was achieved so far.

Supplementary Material Available: Listings of crystallographic details, final fractional atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond distances and bond angles, and torsion angles (9 pages); a table of F_o and F_c values (7 pages). Ordering information is given on any current masthead page.

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A Tetraazamacrocycle Functionalized with Pendant Pyrazole Groups: Synthesis of the Octadentate Ligand 1,4,7,10-Tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L) and Its Transformation to the Ligand 1,4,7-Tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane (L'). Structural Characterizations of the Complexes $[NiL]I_2$, $[NiL'](BPh_4)_2 \cdot 2(CH_3)_2CO$, and $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$

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The reaction of 1-(hydroxymethyl)pyrazole with 1,4,7,10-tetraazacyclododecane in CH_3CN gives the new pyrazole-containing tetraazamacrocyclic ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L). This potentially octadentate ligand gives iron(II), nickel(II), and copper(II) complexes of general formula $[ML]Y_2$ (M = Ni, Y = Br, I, ClO_4; M = Fe, Y = BPh_4; M = Cu, Y = Cl), which have been isolated in the solid state and characterized by means of standard physical-chemical methods. The structure of $[NiL]I_2$ (**1**) in the solid state has been established by X-ray diffraction methods: monoclinic $C2/c$, a = 15.210 (7) Å, b = 11.524 (3) Å, c = 17.829 (8) Å, β = 100.20 (4)°, Z = 4. The complex is six-coordinated, having two pendant arms of the octadentate ligand uncoordinated. The same L ligand reacts with hydrated $NiCl_2$ and respectively hydrated $ZnCl_2$ in an ethanol-acetone solution of $NaBPh_4$, giving the two complexes $[ML'](BPh_4)_2 \cdot n(CH_3)_2CO$ [M = Ni, n = 2 (**2**); M = Zn, n = 1 (**3**)], where L' is the new ligand 1,4,7-tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane originating from L by substitution of an ethoxo group for the pyrazole group in one of the pendant arms. The crystal structures of these two complexes have been determined by X-ray diffraction: **2**, monoclinic $P2_1/n$, a = 20.476 (5) Å, b = 13.581 (9) Å, c = 25.742 (5) Å, β = 99.83 (2)°, Z = 4; **3**, triclinic $P\bar{1}$, a = 13.409 (15) Å, b = 25.286 (9) Å, c = 11.055 (5) Å, α = 102.53 (4)°, β = 113.15 (7)°, γ = 79.89 (7)°, Z = 2. The nickel complex is six-coordinated, with one pyrazole group and the ethoxo group uncoordinated, whereas the zinc complex is seven-coordinated, with the ethoxo group uncoordinated. A possible mechanism of the ligand transformation is discussed.

Introduction

The coordination properties toward metal ions of macrocycles bearing pendant donor groups from the macrocycle skeleton have recently attracted much interest, mainly as the study of such systems may provide a basis for a better knowledge of the metal environment in some metalloenzymes and metalloproteins. A number of functionalized macrocyclic ligands have now been reported, and most of them contain as pendant donors aliphatic amines,[1] pyridyl groups,[2] carboxylic acids,[3] alcohols and phenols,[4] nitriles,[1a,5] and other donor groups.[5c,6] Only recently attempts to functionalize macrocycles with biomimetic donors have suc-

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